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(54) Title : "PROCESS FOR PRODUCING A SLOW-RELEASING BORON FERTILIZER."

(57) Abstract :

This invention relates to a process for the manufacture of a slow releasing boron fertilizer comprising of polyborophosphate compounds. This product has several advantages over the existing boron fertilizers which are water soluble compounds. By virtue of its low water solubility, leaching losses are reduced, toxicity due to overdoses is minimised and transformation to unavailable form is lowered; thereby fertilizer used efficiency is greatly increased.According to the process of the present invention, magnesium oxide is first reacted with phosphoric acid and this is subsequently reacted with the monosodium salt of boric acid. The final reaction occurs at a temperature of around 300`C. The product is an anionic copolymer of borate and phosphate with charge compensated by magnesium and sodium ions.

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THE PATENTS ACT. 1970

COMPLETE

Specification

SECTION 10

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to a process for the manufacture of a slow-releasing boron fertilizer comprising of polyborophosphate compounds. According to the process of the present invention, magnesium oxide is first reacted with phosphoric acid and this is subsequently reacted with the monosodium salt of boric acid, to produce the desired fertilizer. The product is a copolymer of borate and phosphate in which the residual charges on the polymer chains, are neutralised by sodium and magnesium ions.

Compounds which are most widely used today as boron fertilizers, are soluble salts such as borax or boric acid (V. Sauchelli, Trace elements in agriculture, Van Nostrand, New York, 1969). It appears that there is no existing Indian patent on the production of such slow releasing boron fertilizers, which are essentially magnesium sodium polyborophosphates. However, in some countries abroad the synthesis of boron fertilizers of low water solubility have been attempted (S.I. Volfkovich et al. J. appl. Chem. USSR 45, 2245, 1972; US Patent 3,655,357, 1972). In these processes boric acid and phosphoric acid are heated together at various temperatures to produce boron phosphates. Such boron phosphates are, however, known to be highly insoluble and inert compounds and, therefore, their efficiency as fertilizer materials is doubtful.

On the other hand, there are some major drawbacks in using soluble salts as boron fertilizers, for example, extensive leatching losses, the possibility of toxicity due to overdoses and the transformation of the borate to unavailable forms. In principle, these problems can be reduced if the compounds used have low watersolubility but at the same time contain the nutrient ions in a form that is available to plants. In practice, however, this is

difficult to realise since in most of the insoluble boron compounds the boron is not readily available to plants. Increasing the availability usually results in an increase in the water solubility, which is not desirable. Thus, the boron phosphates as well as the borate glass frits are highly non-available sources and consequently are not popular as fertilizers. In the present invention, it has been possible to eliminate this difficulty by producing a polymeric compound which is not only insoluble in water but also contains boron in a completely available form. Manufacturing temperatures are also much lower than that required for the borate glasses and the refractory borophosphates.

The present invention provides a process for the manufacture of slow-releasing boron fertilizer which process comprises (a) neutralising boric acid with sodium carbonate, (b) reacting magnesium oxide with phosphoric acid at 110°C, at a Mg : P ratio of 1 : 2.36, (c) mixing the sodium borate solution obtained from the stage (a) with the magnesium phosphate obtained from stage (b), at a B : P ratio of 1 : 1, and finally (d) heating the mixture at 300°C.

Accordingly, this invention provides a process for producing a magnesium sodium polyborophosphate compound which is water-insoluble, non-toxic, non-hygroscopic and contains boron in a completely available form. The main novel feature of this invention is the reaction of mono-sodium dihydrogen borate with magnesium dihydrogen phosphate to produce a borate-phosphate copolymer. Another novel feature is

the ratio of magnesium salt, and phosphoric acid the boron salt, to be taken, which determines the water solubility as well as the availability of boron to plants. Further, the presence of two cations, viz., the magnesium and sodium ions ensures the desired balance of solubility, in water and in organic complexants. The production of long chain polymers approaching the meta-composition, eliminates the problem of hygroscopicity in the product.

The principle underlying the production of slow-releasing boron fertilizer according to the process of the present invention is that, initially, when magnesium oxide is heated with phosphoric acid, magnesium dihydrogen phosphate is formed. Subsequently, when the monosodium salt of boric acid is added to it and the mixture heated at higher temperatures, polymerisation of the phosphate groups occurs. During polymerisation of the phosphates, the borate ions are incorporated in the linear chains forming P-O-B bonds. The Mg^{2+} and Na^{+} ions occupy positions satisfying the O^{-} valancies along the chain. Dissolution occurs by hydrolytic cleavage of the P-O-P and P-O-B bonds. The substitution of the P atoms by B in the polyphosphate chains, increases the solubility of the polymers since the P-O-B bonds are more readily hydrolysed than the P-O-P. Solubility of these polyborophosphates are, therefore, reduced by the substitution of Mg^{2+} ions in the structure, which serve to cross-link adjacent chains.

Magnesium oxide and phosphoric acid are allowed to react at 110°C to form the dihydrogen phosphate. In another stage, a sus-

pension of boric acid is neutralised with sodium carbonate to pH 11.5, wherein a solution of the monosodium salt of the acid is formed. Subsequently, the borate solution is added to the magnesium phosphate, the mixture is stirred well and heated at 300°C for 60 min. The product is then cooled and ground to a powder.

Magnesium oxide powder containing upto 60.0% Mg, boric acid containing upto 17.4% B and phosphoric acid containing upto 27.8% P may be used as the starting materials. Every 100 g of MgO is treated with phosphoric acid containing 416 g P_2O_5. The amount of H_3PO_4 used here, is in slight excess of that which is stoichiometrically required for forming the $Mg(H_2PO_4)_2$ salt. This excess of acid facilitates dissolution of the MgO for, otherwise, some particles tend to remain undissolved. A Mg : P ratio of 1 : 2.36 is the optimum proportion necessary for forming the $Mg(H_2PO_4)_2$ and at the same time ensuring that too much of free acid does not remain after reaction. Almost any grade and dilution of the acid can be used for the reaction. Commercial acid of 30-40% P_2O_5 is quite suitable though syrupy acid containing 60% P_2O_5, is optimum. The mixture of MgO and H_3PO_4, taken in a porcelain curcible, is heated in a furnace at 110°C for 60 mins. The time of heating will, however, vary with nature of the container, but in general the mixture is to be heated till the solid MgO completely dissolves and a syrupy liquid is obtained. At lower temperatures, the reaction takes a much longer time to complete whereas at higher temperatures, polymerisation of the phosphate occurs. Therefore,

a reaction temperature of 110°C is optimum. In a separate container a solution of monosodium dihydrogen borate is produced by neutralising 2059 ml of 17.54% boric acid suspension with 309 g Na_2CO_3 at room temperature. The concentration of the boric acid must be such as to ensure that after neutralisation, the salt remains soluble. It has been observed that any concentration below 20% H_3BO_3 is suitable. With very dilute solutions, no particular difficulty is encountered, except that an unnecessary amount of free water will be introduced which will again require longer periods of heating. The pH of the solution so obtained, is 11.5. It is subsequently transferred into the vessel containing the magnesium dihydrogen phosphate. The proportion of P : B in this mixture is 1 : 1. Solubility of the ultimate product in water and in solutions of organic complexants (like EDTA, citric acid, DTPA, etc.) is strongly influenced by the ratio of P : B in it. Thus, when the P content is increased by increasing the proportion of $Mg(H_2PO_4)_2$ in the reaction mixture, the product becomes more insoluble in the above complexants; conversely, an increase in the B-content causes the product to become more soluble in the above complexants as well as in water. By maintaining a P : B ratio of 1 : 1, the solubility of the product in water remains very low while at the same time it can be completely dissolved by complexing solutions. These are the characteristics which are desired of the slow-releasing fertilizer. The P : B ratio of the product can be varied within the range 1 : 1.5 to 1 : 0.66 without causing any significant deterioration of its properties.

The reaction mixture of magnesium phosphate and sodium borate is heated at 300°C for 60 mins. These conditions are sufficient to cause almost complete polymerisation to a metaphosphate composition. The product is dehydrated to 100% of the theoretically possible value. Thus, for a reaction mixture containing an equivalent of 100 g of (H_3PO_4 + H_3BO_3), the amount of weight loss after reaction is 23 g. In other words, for every 100 g of MgO reacted with 573 g H_3PO_4 and 360 g H_3BO_3, the loss of weight on heating, is 215 g (excluding the weight loss due to the free water in the system). The same product may also be obtained by heating at any temperature between 250° - 350°C. However, at lower temperatures, much longer heating periods are required and at higher temperatures, the reaction becomes so rapid that it is difficult to control. A reaction temperature of 300°C was, therefore, observed to be optimum. At the end of the reaction period, the product is cooled to room temperature and ground to a powder.

The characteristics of this fertilizer are as follows : It is a white, non-hygroscopic powder containing 6.23% B, 19.38% P, 9.38% Mg, 9.38% Na and with a suspension pH of 8. It is practically insoluble in water but is completely solubilised by 0.1 N HCl, 1 N Citric acid and 1 N ammonium citrate at pH 8.5.

Solubility in these aforementioned reagents indicate that the boron in the fertilizer is in a 100% available form for plant uptake. Experiments reveal that the slow-releasing boron fertilizer is as efficient as borax in its ability to provide boron for plant growth.

Example

Magnesium oxide powder (100 g) was taken in a porcelain dish and 1000 ml of phosphoric acid containing 41.6% P_2O_5 by weight was added to it. The weight of the mixture was recorded. It was then heated in an electric furnace at 110°C for 60 min.

To a beaker containing 361 g H_3BO_3 in 2059 ml water, 309 g Na_2CO_3 was added and stirred till it dissolved completely and the pH of the solution was 11.5. This was added to the preheated magnesium salt and stirred well. The mixture was finally heated at 300°C for 60 min. The weight of the mixture, after heating, was also recorded. The desired degree of polymerisation of the product is obtained when the weight loss corresponds to 23% of the content of (H_3PO_4 + H_3BO_3) in the system. If, after heating, the weight of the sample is observed to be higher, then heating is continued till the desired degree of weight loss is observed. Once the period of heating is calibrated for a particular furnace and for a particular type of container and amount of sample, then all subsequent samples can be heated for that period; recording the initial and final weights is, then, not necessary.

After the heating period was complete, the sample was cooled to room temperature and powdered in a mortar. The material thus obtained has the composition 6.23% B, 19.38% P, 9.38% Mg and 9.38% Na.

We claim : 175597

1. A process for the manufacture of slow-releasing boron fertilizer, which process comprises (a) neutralising boric acid with sodium carbonate, (b) reacting magnesium oxide with phosphoric acid at 110^{o}C, at a Mg : P ratio of 1 : 2.36, (c) mixing the sodium borate solution obtained from the stage (a) with the magnesium phosphate obtained from stage (b), at a B : P ratio of 1 : 1, and finally (d) heating the mixture at 300^{o}C.

2. A process as claimed in claim 1 wherein at stage (a) the boric acid suspension used has any concentration between 12% and 20% by weight H_3BO_3.

3. A process as claimed in any of the preceding claims wherein at stage (a) 309 g of Na_2CO_3 is used for neutralising a suspension of 361 g of boric acid in 2059 ml water.

4. A process as claimed in any of the preceding claims wherein at stage (b) the phosphoric acid used has any concentration between 30% and 60% by weight P_2O_5.

5. A process as claimed in any of the preceding claims wherein at stage (b) the reaction is carried out at a temperature of 110^{o}C for 60 min.

6. A process as claimed in any of the preceding claims wherein at stage (b) the reaction is carried out till the MgO completely dissolves in the acid.

7. A process as claimed in any of the preceding claims wherein the amount of phosphoric acid used is equivalent to 416 g P_2O_5 per 100 g of magnesium oxide.

8. A process as claimed in any of the preceding claims wherein at stage (c) the P : B ratio in the mixture is within a range 1 : 1.5 to 1 : 0.66.

9. A process as claimed in any of the preceding claims wherein at stage (c) the P : B ratio in the mixture is 1 : 1.

10. A process as claimed in any of the preceding claims wherein at stage (d) the mixture is heated at any temperature within a range 250^{o}-$350^{o}C$.

11. A process as claimed in any of the claims 1 to 8 wherein at stage (d) the reaction is carried out at $300^{o}C$ for 60 min.

12. A process as claimed in any of the preceding claims wherein at stage (d) the reaction is continued at $300^{o}C$ until the weight loss due to dehydration corresponds to 23% of the original weight of (H_3PO_4 + H_3BO_3).

13. A process for the manufacture of slow-releasing boron fertilizer substantially as herein described and as illustrated in the example.

Dated this 14th day of May 1991

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14 May 1991

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